

CLAIMS

What is claimed is:

1. A stabilized solution of a p-phenylenediamine free base color developer comprising:
  - a. about 10 to 40 weight percent of a p-phenylenediamine free base color developer selected from the group consisting of N,N-diethyl-2-methyl-p-phenylenediamine, N-ethyl-N-2-(methanesulfonylaminoethyl)-2-methyl-p-phenylenediamine, N-ethyl-N-2-(hydroxyethyl)-2-methyl-p-phenylenediamine and mixtures thereof;
  - b. about 40 to 70 weight percent of at least one hydroxy-containing organic solvent for the p-phenylenediamine free base color developer; and
  - c. about 1 to 40 weight percent of a p-phenylenediamine free base color developer preservative, and wherein the weight percentages are based on the total weight of the stabilized solution.
2. The stabilized solution of claim 1 wherein said hydroxy-containing organic solvent is selected from the group consisting of 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-methyl-1-butanol, and 3-methyl-2-butanol, ethylene glycol, propylene glycol, 1,4-butanediol, 1,3-butanediol, 2-methyl-1,3-propanediol, 1,4-cyclohexanediethanol, diethylene glycol, triethylene glycol, polyethylene glycol selected from the group consisting of PEG-200, PEG-300, PEG-400, and PEG-600; 2-methoxyethanol, 2-ethoxyethanol, 2-propoxyethanol, 2-isopropoxyethanol, 2-butoxyethanol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, 3-methoxy-1-butanol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-i-propyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, dioxane, glycerol, 3-methoxy-1,2-propanediol, 3-ethoxy-1,2-propanediol, and mixtures of these solvents.
3. The stabilized solution of claim 1 wherein said hydroxy-containing organic solvent is selected from the group consisting of 2-propanol, 2-isopropoxyethanol, diethylene glycol, ethylene glycol, propylene glycol, PEG-200 and mixtures of these solvents.

4. The stabilized solution of claim 1 wherein said solution comprises from about 15 to 35 weight percent, p-phenylenediamine free base based on the total weight of the stabilized solution.
5. The stabilized solution of claim 1 wherein said solution comprises from about 1 to about 30 weight percent of a preservative.
6. The stabilized solution of claim 1 wherein said solution comprises from about 2 to about 15 weight percent of a preservative.
7. The stabilized solution of claim 1 wherein said preservative is selected from the group consisting of sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, sodium metabisulfite, potassium metabisulfite, carbonyl-sulfite adducts, hydroxylamines, N,N-disubstituted hydroxylamines, hydroxamic acids, hydrazines, hydrazides, aminoketones, phenols, amino acids, mono- and polysaccharides, mono-, di-, and polyamines, ascorbic acid, alcohols, oximes, nitroxy radicals and mixtures of these preservatives.
- 15 8. The stabilized solution of claim 7 wherein said preservative is selected from the group consisting of N,N-dialkylhydroxylamine, N,N-diethylhydroxylamine, ascorbic acid, erythrobic acid, sodium sulfite, potassium sulfite, and mixtures of these preservatives.
9. The stabilized solution of claim 1 further comprising from about 4 to 12 weight percent water.
- 20 10. A stabilized solution of a p-phenylenediamine free base color developer comprising:
  - a. about 15 to 35 weight percent of a p-phenylenediamine free base color developer selected from the group consisting of N,N-diethyl-2-methyl-p-phenylenediamine, N-ethyl-N-2-(methanesulfonylaminoethyl)-2-methyl-p-phenylenediamine, N-ethyl-N-2-(hydroxyethyl)-2-methyl-p-phenylenediamine and mixtures thereof;
  - b. about 40 to 70 weight percent of at least one hydroxy-containing organic solvent for the p-phenylenediamine free base color developer selected from the group consisting of 2-propanol, 2-isopropoxyethanol, diethylene glycol, ethylene glycol, propylene glycol, PEG-200 and mixtures of these solvents; and

- c. about 1 to 40 weight percent of a p-phenylenediamine free base color developer preservative selected from the group consisting of N,N-diethylhydroxylamine, ascorbic acid, erythrobic acid, sodium sulfite, potassium sulfite, and mixtures of these preservatives, and wherein the weight percentages are based on the total weight of the stabilized solution.
- 5 11. A stabilized solution of a p-phenylenediamine free base color developer consisting essentially of:
  - a. about 10 to 40 weight percent of a p-phenylenediamine free base color developer selected from the group consisting of N,N-diethyl-2-methyl-p-phenylenediamine, N-ethyl-N-2-(methanesulfonylaminoethyl)-2-methyl-p-phenylenediamine, N-ethyl-N-2-(hydroxyethyl)-2-methyl-p-phenylenediamine and mixtures thereof;
  - 10 b. about 40 to 70 weight percent of at least one hydroxy-containing organic solvent for the p-phenylenediamine free base color developer; and
  - c. about 1 to 40 weight percent of a p-phenylenediamine free base color developer preservative, and wherein the weight percentages are based on the total weight of the stabilized solution.
- 15 12. The stabilized solution of claim 11 wherein said hydroxy-containing organic solvent is selected from the group consisting of 2-propanol, 2-isoproxyethanol, diethylene glycol, ethylene glycol, propylene glycol, PEG-200 and mixtures of these solvents.
- 20 13. The stabilized solution of claim 11 wherein said solution comprises from about 15 to 35 weight percent, p-phenylenediamine free base based on the total weight of the stabilized solution.
- 25 14. The stabilized solution of claim 11 wherein said preservative is selected from the group consisting of N,N-dialkylhydroxylamine, N,N-diethylhydroxylamine, ascorbic acid, erythrobic acid, sodium sulfite, potassium sulfite, and mixtures of these preservatives.
- 30 15. A solid, stabilized p-phenylenediamine free base composition comprising:
  - a. from 50 to about 99 weight percent of a p-phenylenediamine free base color developer; and

- b. from about 1 to 50 weight percent of a p-phenylenediamine free base color developer preservative, and wherein the weight percentages are based on the total weight of the solid, stabilized p-phenylenediamine free base composition.
- 16. The solid, stabilized composition of claim 15 wherein said p-phenylenediamine free base color developer is from about 80 to 99 weight % and said preservative is from about 1 to 20 weight % of the composition.
- 5 17. The solid, stabilized composition of claim 15 wherein said p-phenylenediamine free base color developer is selected from the group consisting of N-ethyl-N-2-(methanesulfonylaminoethyl)-2-methyl-p-phenylenediamine, N-ethyl-N-2-(hydroxyethyl)-2-methyl-p-phenylenediamine and mixtures thereof.
- 10 18. The stabilized solution of claim 15 wherein said preservative is selected from the group consisting of sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, sodium metabisulfite, potassium metabisulfite, carbonyl-sulfite adducts, hydroxylamines, N,N-disubstituted hydroxylamines, hydroxamic acids, hydrazines, hydrazides, aminoketones, phenols, amino acids, mono- and polysaccharides, mono-, di-, and polyamines, ascorbic acid, alcohols, oximes, nitroxy radicals and mixtures of these preservatives.
- 15 19. The stabilized solution of claim 15 wherein said preservative is selected from the group consisting of N,N-dialkylhydroxylamine, N,N-diethylhydroxylamine, ascorbic acid, erythrobic acid, sodium sulfite, potassium sulfite, and mixtures of these preservatives.
- 20 20. A process for preparing a stabilized solution of a p-phenylenediamine free base color developer which comprises the steps of:
  - a. hydrogenating a nitro or nitroso precursor compound of the p-phenylenediamine free base color developer under hydrogenation conditions of pressure and temperature and in the presence of a heterogeneous, hydrogenation catalyst and at least one photographically inactive, water-miscible or water-soluble, hydroxy-containing, organic solvent of the color developing agent in free base form to obtain a mixture of the heterogeneous catalyst in a solution of p-phenylenediamine color developer free base and organic solvent;
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- b. separating the heterogeneous catalyst from the solution of p-phenylenediamine color developer free base and organic solvent; and
- c. adding a p-phenylenediamine color developer free base preservative to the solution obtained in step (b).

5 21. The process of claim 20 wherein said precursor is selected from the group consisting of 4-nitroso or nitro-3-methyl-N,N-diethylaniline, 4-nitroso or nitro-3-methyl-N-ethyl-N-(2-methanesulfonamidoethyl)aniline, 4-nitroso or nitro-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline and mixtures thereof.

10 22. The process of claim 20 wherein said precursor is selected from the group consisting of 4-nitroso-3-methyl-N,N-diethylaniline, 4-nitroso-3-methyl-N-ethyl-N-(2-methanesulfonamidoethyl)aniline or 4-nitroso-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline.

15 23. The process of claim 20 wherein said hydroxy-containing organic solvent is selected from the group consisting of 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-methyl-1-butanol, and 3-methyl-2-butanol, ethylene glycol, propylene glycol, 1,4-butanediol, 1,3-butanediol, 2-methyl-1,3-propanediol, 1,4-cyclohexanediethanol, diethylene glycol, triethylene glycol, polyethylene glycol selected from the group consisting of PEG-200, PEG-300, PEG-400, and PEG-600; 2-methoxyethanol, 2-ethoxyethanol, 2-propoxyethanol, 2-isopropoxyethanol, 2-butoxyethanol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, 3-methoxy-1-butanol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-i-propyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, dioxane, glycerol, 3-methoxy-1,2-propanediol, 3-ethoxy-1,2-propanediol, and mixtures of these solvents.

20 24. The stabilized solution of claim 23 wherein said hydroxy-containing organic solvent is selected from the group consisting of 2-propanol, 2-isopropoxyethanol, diethylene glycol, ethylene glycol, propylene glycol, PEG-200 and mixtures of these solvents.

25 25. The stabilized solution of claim 23 wherein said preservative is selected from the group consisting of sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, sodium metabisulfite, potassium metabisulfite, carbonyl-sulfite adducts,

hydroxylamines, N,N-disubstituted hydroxylamines, hydroxamic acids, hydrazines, hydrazides, aminoketones, phenols, amino acids, mono- and polysaccharides, mono-, di-, and polyamines, ascorbic acid, alcohols, oximes, nitroxy radicals and mixtures of these preservatives.

5 26. A process for preparing a stabilized solution of a p-phenylenediamine free base color developer which comprises the steps of:

- a. hydrogenating a nitro or nitroso precursor compound of the p-phenylenediamine color developer free base in the presence of a hydrogenation catalyst and a first solvent selected from the group consisting of alkanols containing 1 to 6 carbon atoms, ethers containing 2 to 6 carbon atoms and mixtures thereof and under hydrogenation conditions of pressure and temperature to obtain a first solution of p-phenylenediamine color developer free base;
- b. separating the heterogeneous catalyst from the first solution of p-phenylenediamine color developer free base;
- c. mixing a second solvent selected from at least one photographically inactive water-miscible or water-soluble, hydroxy-containing, organic solvent of the color developing agent in free base form with the first solution to obtain a second solution, and wherein the organic solvent has a boiling point at least 5°C higher than the first solvent;
- d. distilling said first solvent from the second solution; and
- e. adding a p-phenylenediamine color developer free base preservative to at least one of the solutions.

20 27. The process of claim 26 wherein said precursor compound is selected from the group consisting of 4-nitroso-3-methyl-N,N-diethylaniline, 4-nitroso-3-methyl-N-ethyl-N-(2-methanesulfonamidoethyl)aniline, 4-nitroso-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline and mixtures thereof, and said p-phenylenediamine color developer free base is selected from the group consisting of N,N-diethyl-2-methyl-p-phenylenediamine, N-ethyl-N-2-(methanesulfonylaminoethyl)-2-methyl-p-phenylenediamine, N-ethyl-N-2-(hydroxyethyl)-2-methyl-p-phenylenediamine and mixtures thereof.

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28. The process of claim 26 wherein said first solvent is selected from the group consisting of methanol, ethanol, tetrahydrofuran, 1-propanol, 2-propanol and mixtures thereof.
29. The process of claim 26 wherein said second solvent is selected from the group consisting of 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 1-pentanol, 2-pentanol, 3-methyl-1-butanol, and 3-methyl-2-butanol, ethylene glycol, propylene glycol, 1,4-butanediol, 1,3-butanediol, 2-methyl-1,3-propanediol, 1,4-cyclohexanediethanol, diethylene glycol, triethylene glycol, polyethylene glycol selected from the group consisting of PEG-200, PEG-300, PEG-400, and PEG-600; 2-methoxyethanol, 2-ethoxyethanol, 2-propoxyethanol, 2-isopropoxyethanol, 2-butoxyethanol, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, 3-methoxy-1-butanol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-n-propyl ether, diethylene glycol mono-i-propyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, dioxane, glycerol, 3-methoxy-1,2-propanediol, 3-ethoxy-1,2-propanediol, and mixtures of these solvents.
30. The process of claim 29 wherein said second solvent is selected from the group consisting of 2-isopropoxyethanol, diethylene glycol, ethylene glycol, propylene glycol, PEG-200 and mixtures of these solvents.
31. The process of claim 26 wherein said preservative is selected from the group consisting of N,N-diethylhydroxylamine, ascorbic acid, erythrobic acid, sodium sulfite, potassium sulfite, and mixtures of these preservatives and said preservative is added to said first solution.
32. The stabilized solution of claim 26 wherein said preservative is selected from the group consisting of N,N-dialkylhydroxylamine, N,N-diethylhydroxylamine, ascorbic acid, erythrobic acid, sodium sulfite, potassium sulfite, and mixtures of these preservatives and said preservative is added to said second solution.
33. A process for preparing a stabilized solution of a p-phenylenediamine free base color developer which comprises the steps of:
  - a. hydrogenating a nitro or nitroso precursor compound of the p-phenylenediamine color developer free base in the presence of a hydrogenation catalyst and a first solvent selected from the group consisting of alkanols containing

1 to 6 carbon atoms, ethers containing 2 to 6 carbon atoms and mixtures thereof and under hydrogenation conditions of pressure and temperature to obtain a first solution of p-phenylenediamine color developer free base;

5       b. separating the heterogeneous catalyst from the first solution of p-phenylenediamine color developer free base;

c. crystallizing the p-phenylenediamine free base in said first solution;

d. recovering the crystallized p-phenylenediamine color developer;

10       e. dissolving the crystallized p-phenylenediamine color developer in a second solvent selected from the group consisting of at least one photographically inactive water-miscible or water-soluble, hydroxy-containing, organic solvent for the color developing agent in free base form to form a second solution; and

15       f. adding a p-phenylenediamine color developer free base preservative to the second solution.

34. The process of claim 33 wherein said precursor compound is selected from the group consisting of 4-nitroso-3-methyl-N-ethyl-N-(2-methanesulfonamidoethyl)aniline, 4-nitroso-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline and mixtures thereof, and said p-phenylenediamine color developer free base is selected from the group consisting of N-ethyl-N-2-(methanesulfonylaminoethyl)-2-methyl-p-phenylenediamine, N-ethyl-N-2-(hydroxyethyl)-2-methyl-p-phenylenediamine and mixtures thereof.

20       35. The process of claim 34 wherein second solvent is selected from the group consisting of 2-propanol, 2-isopropoxyethanol, diethylene glycol, ethylene glycol, propylene glycol, PEG-200 and mixtures of these solvents.

25       36. The process of claim 33 wherein said preservative is selected from the group consisting of N,N-diethylhydroxylamine, ascorbic acid, erythrobic acid, sodium sulfite, potassium sulfite, and mixtures of these preservatives.

37. A process for preparing a solid stabilized p-phenylenediamine free base color developer which comprises the steps of:

30       a. hydrogenating a nitro or nitroso precursor compound of the p-phenylenediamine color developer free base in the presence of a hydrogenation catalyst and a solvent selected from the group consisting of alkanols containing 1 to

6 carbon atoms, ethers containing 2 to 6 carbon atoms and mixtures thereof and under hydrogenation conditions of pressure and temperature to obtain a solution of p-phenylenediamine color developer free base;

5       b. separating the heterogeneous catalyst from the solution of p-phenylenediamine color developer free base;

      c. crystallizing the p-phenylenediamine free base in said first solution;

      d. recovering the crystallized p-phenylenediamine color developer;

      e. adding a non-volatile preservative to the recovered crystallized p-phenylenediamine color developer free base; and

10      f. drying the p-phenylenediamine color developer in the presence of said preservative.

38. The process of claim 37 wherein said precursor compound is selected from the group consisting of 4-nitroso-3-methyl-N-ethyl-N-(2-methanesulfonamidoethyl)aniline, 4-nitroso-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline and mixtures thereof, and said p-phenylenediamine color developer free base is selected from the group consisting of N-ethyl-N-2-(methanesulfonylaminoethyl)-2-methyl-p-phenylenediamine, 15 N-ethyl-N-2-(hydroxyethyl)-2-methyl-p-phenylenediamine and mixtures thereof.

39. The process of claim 37 wherein said preservative is selected from the group consisting of N,N-diethylhydroxylamine, ascorbic acid, erythrobic acid, sodium sulfite, potassium sulfite, and mixtures of these preservatives.

20      40. The process of claim 37 wherein said heterogeneous catalyst is separated from the solution of p-phenylenediamine color developer free base by filtration.

41. The process of claim 37 wherein said solvent is selected from the group consisting of methanol, ethanol, tetrahydrofuran, 1-propanol, 2-propanol and mixtures thereof.